METHOD 204A--VOLATILE ORGANIC COMPOUNDS CONTENT IN LIQUID INPUT STREAM

1. SCOPE AND APPLICATION

1.1 Applicability. This procedure is applicable for determining the input of volatile organic compounds (VOC). It is intended to be used in the development of liquid/gas protocols for determining VOC capture efficiency (CE) for surface coating and printing operations.

1.2 Principle. The amount of VOC introduced to the process (L) is the sum of the products of the weight (W) of each VOC containing liquid (ink, paint, solvent, etc.) used and its VOC content (V).

1.3 Sampling Requirements. A CE test shall consist of at least three sampling runs. Each run shall cover at least one complete production cycle, but shall be at least 3 hours long. The sampling time for each run need not exceed 8 hours, even if the production cycle has not been completed. Alternative sampling times may be used with the approval of the Administrator.

2. SUMMARY OF METHOD

The amount of VOC containing liquid introduced to the process is determined as the weight difference of the feed material before and after each sampling run. The VOC content of the liquid input material is determined by volatilizing a small aliquot of the material and analyzing the volatile material using a flame ionization analyzer (FIA). A sample of each VOC

containing liquid is analyzed with a FIA to determine V.

3. SAFETY

Because this procedure is often applied in highly explosive areas, caution and care should be exercised in choosing, installing, and using the appropriate equipment.

4. EQUIPMENT AND SUPPLIES

Mention of trade names or company products does not constitute endorsement. All gas concentrations (percent, ppm) are by volume, unless otherwise noted.

4.1 Liquid Weight.

4.1.1 Balances/Digital Scales. To weigh drums of VOC containing liquids to within 0.2 lb or 1.0 percent of the total weight of VOC liquid used.

4.1.2 Volume Measurement Apparatus (Alternative). Volume meters, flow meters, density measurement equipment, etc., as needed to achieve the same accuracy as direct weight measurements.

4.2 VOC Content (FIA Technique). The liquid sample analysis system is shown in Figures 204A-1 and 204A-2. The following equipment is required:

4.2.1 Sample Collection Can. An appropriately-sized metal can to be used to collect VOC containing materials. The can must be constructed in such a way that it can be grounded to the coating container.

4.2.2 Needle Valves. To control gas flow.

4.2.3 Regulators. For carrier gas and calibration gas cylinders.

4.2.4 Tubing. Teflon or stainless steel tubing with diameters and lengths determined by connection requirements of equipment. The tubing between the sample oven outlet and the FIA shall be heated to maintain a temperature of 120 ± 5°C.

4.2.5 Atmospheric Vent. A tee and 0- to 0.5-liter/min rotameter placed in the sampling line between the carrier gas cylinder and the VOC sample vessel to release the excess carrier gas. A toggle valve placed between the tee and the rotameter facilitates leak tests of the analysis system.

4.2.6 Thermometer. Capable of measuring the temperature of the hot water bath to within 1°C.

4.2.7 Sample Oven. Heated enclosure, containing calibration gas coil heaters, critical orifice, aspirator, and other liquid sample analysis components, capable of maintaining a temperature of 120 ± 5°C.

4.2.8 Gas Coil Heaters. Sufficient lengths of stainless steel or Teflon tubing to allow zero and calibration gases to be heated to the sample oven temperature before entering the critical orifice or aspirator.

4.2.9 Water Bath. Capable of heating and maintaining a sample vessel temperature of 100 ± 5°C.

4.2.10 Analytical Balance. To measure ±0.001 g.

4.2.11 Disposable Syringes. 2-cc or 5-cc.

4.2.12 Sample Vessel. Glass, 40-ml septum vial. A separate vessel is needed for each sample.

4.2.13 Rubber Stopper. Two-hole stopper to accommodate 3.2-mm (1/8-in.) Teflon tubing, appropriately sized to fit the opening of the sample vessel. The rubber stopper should be wrapped in Teflon tape to provide a tighter seal and to prevent any reaction of the sample with the rubber stopper. Alternatively, any leak-free closure fabricated of nonreactive materials and accommodating the necessary tubing fittings may be used.

4.2.14 Critical Orifices. Calibrated critical orifices capable of providing constant flow rates from 50 to 250 ml/min at known pressure drops. Sapphire orifice assemblies (available from O'Keefe Controls Company) and glass capillary tubing have been found to be adequate for this application.

4.2.15 Vacuum Gauge. Zero to 760-mm (0- to 30-in.) Hg U-Tube manometer or vacuum gauge.

4.2.16 Pressure Gauge. Bourdon gauge capable of measuring the maximum air pressure at the aspirator inlet (e.g., 100 psig).

4.2.17 Aspirator. A device capable of generating sufficient vacuum at the sample vessel to create critical flow through the calibrated orifice when sufficient air pressure is present at the aspirator inlet. The aspirator must also provide

sufficient sample pressure to operate the FIA. The sample is
also mixed with the dilution gas within the aspirator.

4.2.18 **Soap Bubble Meter.** Of an appropriate size to
calibrate the critical orifices in the system.

4.2.19 **Organic Concentration Analyzer.** An FIA with a span
value of 1.5 times the expected concentration as propane;
however, other span values may be used if it can be demonstrated
that they would provide more accurate measurements. The FIA
instrument should be the same instrument used in the gaseous
analyses adjusted with the same fuel, combustion air, and sample
back-pressure (flow rate) settings. The system shall be capable
of meeting or exceeding the following specifications:

4.2.19.1 **Zero Drift.** Less than ±3.0 percent of the span
value.

4.2.19.2 **Calibration Drift.** Less than ±3.0 percent of the
span value.

4.2.19.3 **Calibration Error.** Less than ±5.0 percent of the
calibration gas value.

4.2.20 **Integrator/Data Acquisition System.** An analog or
digital device or computerized data acquisition system used to
integrate the FIA response or compute the average response and
record measurement data. The minimum data sampling frequency for
computing average or integrated values is one measurement value
every 5 seconds. The device shall be capable of recording
average values at least once per minute.

4.2.21 Chart Recorder (Optional). A chart recorder or similar device is recommended to provide a continuous analog display of the measurement results during the liquid sample analysis.

5. REAGENTS AND STANDARDS

5.1 Calibration and Other Gases. Gases used for calibration, fuel, and combustion air (if required) are contained in compressed gas cylinders. All calibration gases shall be traceable to National Institute of Standards and Technology standards and shall be certified by the manufacturer to ±1 percent of the tag value. Additionally, the manufacturer of the cylinder should provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ±2 percent from the certified value. For calibration gas values not generally available, dilution systems calibrated using Method 205 may be used. Alternative methods for preparing calibration gas mixtures may be used with the approval of the Administrator.

5.1.1 Fuel. The FIA manufacturer's recommended fuel should be used. A 40 percent H_2/60 percent He or 40 percent H_2/60 percent N_2 gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value. Other mixtures may be used provided the tester can demonstrate to the Administrator that there is no oxygen synergism effect.

5.1.2 Carrier Gas. High purity air with less than

1 ppm of organic material (as propane) or less than
0.1 percent of the span value, whichever is greater.

    5.1.3 **FIA Linearity Calibration Gases.** Low-, mid-, and
high-range gas mixture standards with nominal propane
concentrations of 20-30, 45-55, and 70-80 percent of the span
value in air, respectively. Other calibration values and other
span values may be used if it can be shown to the Administrator's
satisfaction that equally accurate measurements would be
achieved.

    5.1.4 **System Calibration Gas.** Gas mixture standard
containing propane in air, approximating the undiluted VOC
concentration expected for the liquid samples.

    6.   **SAMPLE COLLECTION, PRESERVATION AND STORAGE**

    6.1 Samples must be collected in a manner that prevents or
minimizes loss of volatile components and that does not
contaminate the coating reservoir.

    6.2 Collect a 100-ml or larger sample of the VOC containing
liquid mixture at each application location at the beginning and
end of each test run. A separate sample should be taken of each
VOC containing liquid added to the application mixture during the
test run. If a fresh drum is needed during the sampling run,
then obtain a sample from the fresh drum.

    6.3 When collecting the sample, ground the sample container
to the coating drum. Fill the sample container as close to the

rim as possible to minimize the amount of headspace.

6.4 After the sample is collected, seal the container so the sample cannot leak out or evaporate.

6.5 Label the container to clearly identify the contents.

7. QUALITY CONTROL

7.1 Required instrument quality control parameters are found in the following sections:

7.1.1 The FIA system must be calibrated as specified in section 8.1.

7.1.2 The system drift check must be performed as specified in section 8.2.

7.2 Audits.

7.2.1 Audit Procedure. Concurrently, analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for compliance samples and the EPA audit sample. If this condition is met, auditing of subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

7.2.2 Audit Samples and Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for

compliance tests. The availability of audit samples may be
obtained by writing:

> Source Test Audit Coordinator (STAC) (MD-77B)
> Quality Assurance Division
> Atmospheric Research and Exposure Assessment Laboratory
> U.S. Environmental Protection Agency
> Research Triangle Park, NC 27711

or by calling the STAC at (919) 541-7834. The request for the
audit sample must be made at least 30 days prior to the scheduled
compliance sample analysis.

7.2.3 Audit Results. Calculate the audit sample
concentration according to the calculation procedure described in
the audit instructions included with the audit sample. Fill in
the audit sample concentration and the analyst's name on the
audit response form included with the audit instructions. Send
one copy to the EPA Regional Office or the appropriate
enforcement agency, and a second copy to the STAC. The EPA
Regional Office or the appropriate enforcement agency will report
the results of the audit to the laboratory being audited.
Include this response with the results of the compliance samples
in relevant reports to the EPA Regional Office or the appropriate
enforcement agency.

8. CALIBRATION AND STANDARDIZATION

8.1 FIA Calibration and Linearity Check. Make necessary
adjustments to the air and fuel supplies for the FIA and ignite
the burner. Allow the FIA to warm up for the period recommended
by the manufacturer. Inject a calibration gas into the

measurement system and adjust the back-pressure regulator to the value required to achieve the flow rates specified by the manufacturer. Inject the zero- and the high-range calibration gases and adjust the analyzer calibration to provide the proper responses. Inject the low- and mid-range gases and record the responses of the measurement system. The calibration and linearity of the system are acceptable if the responses for all four gases are within 5 percent of the respective gas values. If the performance of the system is not acceptable, repair or adjust the system and repeat the linearity check. Conduct a calibration and linearity check after assembling the analysis system and after a major change is made to the system.

8.2 Systems Drift Checks. After each sample, repeat the system calibration checks in section 9.2.7 before any adjustments to the FIA or measurement system are made. If the zero or calibration drift exceeds ±3 percent of the span value, discard the result and repeat the analysis. Alternatively, recalibrate the FIA as in section 8.1 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test period). The data that results in the lowest CE value shall be reported as the results for the test run.

8.3 Critical Orifice Calibration.

8.3.1 Each critical orifice must be calibrated at the specific operating conditions under which it will be used. Therefore, assemble all components of the liquid sample analysis

system as shown in Figure 204A-3. A stopwatch is also required.

8.3.2 Turn on the sample oven, sample line, and water bath heaters, and allow the system to reach the proper operating temperature. Adjust the aspirator to a vacuum of 380 mm (15 in.) Hg vacuum. Measure the time required for one soap bubble to move a known distance and record barometric pressure.

8.3.3 Repeat the calibration procedure at a vacuum of 406 mm (16 in.) Hg and at 25-mm (1-in.) Hg intervals until three consecutive determinations provide the same flow rate. Calculate the critical flow rate for the orifice in ml/min at standard conditions. Record the vacuum necessary to achieve critical flow.

9. PROCEDURE

9.1 Determination of Liquid Input Weight.

9.1.1 Weight Difference. Determine the amount of material introduced to the process as the weight difference of the feed material before and after each sampling run. In determining the total VOC containing liquid usage, account for:

(a) The initial (beginning) VOC containing liquid mixture.

(b) Any solvent added during the test run.

(c) Any coating added during the test run.

(d) Any residual VOC containing liquid mixture remaining at the end of the sample run.

9.1.1.1 Identify all points where VOC containing liquids are introduced to the process. To obtain an accurate measurement of VOC containing liquids, start with an empty fountain (if

applicable). After completing the run, drain the liquid in the fountain back into the liquid drum (if possible) and weigh the drum again. Weigh the VOC containing liquids to ±0.5 percent of the total weight (full) or ±1.0 percent of the total weight of VOC containing liquid used during the sample run, whichever is less. If the residual liquid cannot be returned to the drum, drain the fountain into a preweighed empty drum to determine the final weight of the liquid.

9.1.1.2 If it is not possible to measure a single representative mixture, then weigh the various components separately (e.g., if solvent is added during the sampling run, weigh the solvent before it is added to the mixture). If a fresh drum of VOC containing liquid is needed during the run, then weigh both the empty drum and fresh drum.

9.1.2 Volume Measurement (Alternative). If direct weight measurements are not feasible, the tester may use volume meters or flow rate meters and density measurements to determine the weight of liquids used if it can be demonstrated that the technique produces results equivalent to the direct weight measurements. If a single representative mixture cannot be measured, measure the components separately.

9.2 Determination of VOC Content in Input Liquids

9.2.1 Assemble the liquid VOC content analysis system as shown in Figure 204A-1.

9.2.2 Permanently identify all of the critical orifices that may be used. Calibrate each critical orifice under the

expected operating conditions (i.e., sample vacuum and temperature) against a volume meter as described in section 8.3.

9.2.3 Label and tare the sample vessels (including the stoppers and caps) and the syringes.

9.2.4 Install an empty sample vessel and perform a leak test of the system. Close the carrier gas valve and atmospheric vent and evacuate the sample vessel to 250 mm (10 in.) Hg absolute or less using the aspirator. Close the toggle valve at the inlet to the aspirator and observe the vacuum for at least 1 minute. If there is any change in the sample pressure, release the vacuum, adjust or repair the apparatus as necessary, and repeat the leak test.

9.2.5 Perform the analyzer calibration and linearity checks according to the procedure in section 5.1. Record the responses to each of the calibration gases and the back-pressure setting of the FIA.

9.2.6 Establish the appropriate dilution ratio by adjusting the aspirator air supply or substituting critical orifices. Operate the aspirator at a vacuum of at least 25 mm (1 in.) Hg greater than the vacuum necessary to achieve critical flow. Select the dilution ratio so that the maximum response of the FIA to the sample does not exceed the high-range calibration gas.

9.2.7 Perform system calibration checks at two levels by introducing compressed gases at the inlet to the sample vessel while the aspirator and dilution devices are operating. Perform these checks using the carrier gas (zero concentration) and the

system calibration gas. If the response to the carrier gas exceeds ±0.5 percent of span, clean or repair the apparatus and repeat the check. Adjust the dilution ratio as necessary to achieve the correct response to the upscale check, but do not adjust the analyzer calibration. Record the identification of the orifice, aspirator air supply pressure, FIA back-pressure, and the responses of the FIA to the carrier and system calibration gases.

9.2.8 After completing the above checks, inject the system calibration gas for approximately 10 minutes. Time the exact duration of the gas injection using a stopwatch. Determine the area under the FIA response curve and calculate the system response factor based on the sample gas flow rate, gas concentration, and the duration of the injection as compared to the integrated response using Equations 204A-2 and 204A-3.

9.2.9 Verify that the sample oven and sample line temperatures are 120 ± 5°C and that the water bath temperature is 100 ± 5°C.

9.2.10 Fill a tared syringe with approximately 1 g of the VOC containing liquid and weigh it. Transfer the liquid to a tared sample vessel. Plug the sample vessel to minimize sample loss. Weigh the sample vessel containing the liquid to determine the amount of sample actually received. Also, as a quality control check, weigh the empty syringe to determine the amount of material delivered. The two coating sample weights should agree

within 0.02 g. If not, repeat the procedure until an acceptable sample is obtained.

9.2.11 Connect the vessel to the analysis system. Adjust the aspirator supply pressure to the correct value. Open the valve on the carrier gas supply to the sample vessel and adjust it to provide a slight excess flow to the atmospheric vent. As soon as the initial response of the FIA begins to decrease, immerse the sample vessel in the water bath. (Applying heat to the sample vessel too soon may cause the FIA response to exceed the calibrated range of the instrument and, thus, invalidate the analysis.)

9.2.12 Continuously measure and record the response of the FIA until all of the volatile material has been evaporated from the sample and the instrument response has returned to the baseline (i.e., response less than 0.5 percent of the span value). Observe the aspirator supply pressure, FIA back-pressure, atmospheric vent, and other system operating parameters during the run; repeat the analysis procedure if any of these parameters deviate from the values established during the system calibration checks in section 9.2.7. After each sample, perform the drift check described in section 8.2. If the drift check results are acceptable, calculate the VOC content of the sample using the equations in section 11.2. Alternatively, recalibrate the FIA as in section 8.1 and report the results using both sets of calibration data (i.e., data determined prior to the test period and data determined following the test

period). The data that results in the lowest CE value shall be reported as the results for the test run. Integrate the area under the FIA response curve, or determine the average concentration response and the duration of sample analysis.

10. DATA ANALYSIS AND CALCULATIONS

10.1 Nomenclature.

A_L = area under the response curve of the liquid sample, area count.

A_S = area under the response curve of the calibration gas, area count.

C_S = actual concentration of system calibration gas, ppm propane.

K = 1.830×10^{-9} g/(ml-ppm).

L = total VOC content of liquid input, kg.

M_L = mass of liquid sample delivered to the sample vessel, g.

q = flow rate through critical orifice, ml/min.

RF = liquid analysis system response factor, g/area count.

$\mathbf{2}_S$ = total gas injection time for system calibration gas during integrator calibration, min.

V_{Fj} = final VOC fraction of VOC containing liquid j.

V_{Ij} = initial VOC fraction of VOC containing liquid j.

V_{Aj} = VOC fraction of VOC containing liquid j added during the run.

V = VOC fraction of liquid sample.

W_{Fj} = weight of VOC containing liquid j remaining at end of the run, kg.

W_{Ij} = weight of VOC containing liquid j at beginning of the run, kg.

W_{Aj} = weight of VOC containing liquid j added during the run, kg.

10.2 Calculations

10.2.1 Total VOC Content of the Input VOC Containing Liquid.

$$L = \sum_{j=1}^{n} V_{Ij} \ W_{Ij} \ - \ \sum_{j=1}^{n} V_{Fj} \ W_{Fj} \ + \ \sum_{j=1}^{n} \ V_{Aj} \ W_{Aj} \qquad \text{Eq. 204A-1}$$

10.2.2 Liquid Sample Analysis System Response Factor for Systems Using Integrators, Grams/Area Count.

$$RF = \frac{C_S \ q \ \theta_S \ K}{A_S} \qquad \text{Eq. 204A-2}$$

10.2.3 VOC Content of the Liquid Sample.

$$V = \frac{A_L \ RF}{M_L} \qquad \text{Eq. 204A-3}$$

11. METHOD PERFORMANCE

The measurement uncertainties are estimated for each VOC containing liquid as follows: W = ±2.0 percent and V = ±4.0 percent. Based on these numbers, the probable uncertainty for L is estimated at about ±4.5 percent for each VOC containing liquid.
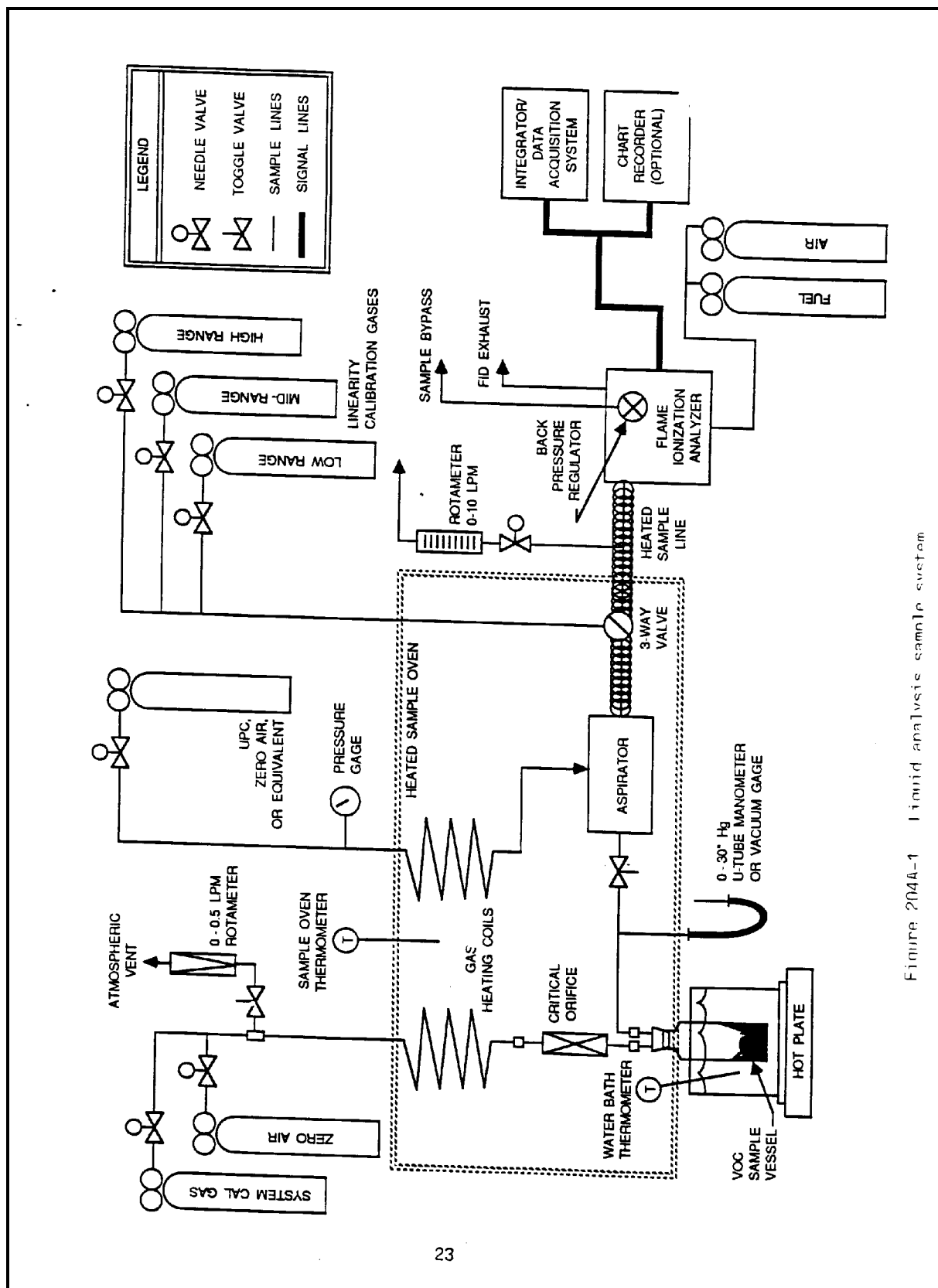
12. DIAGRAMS.

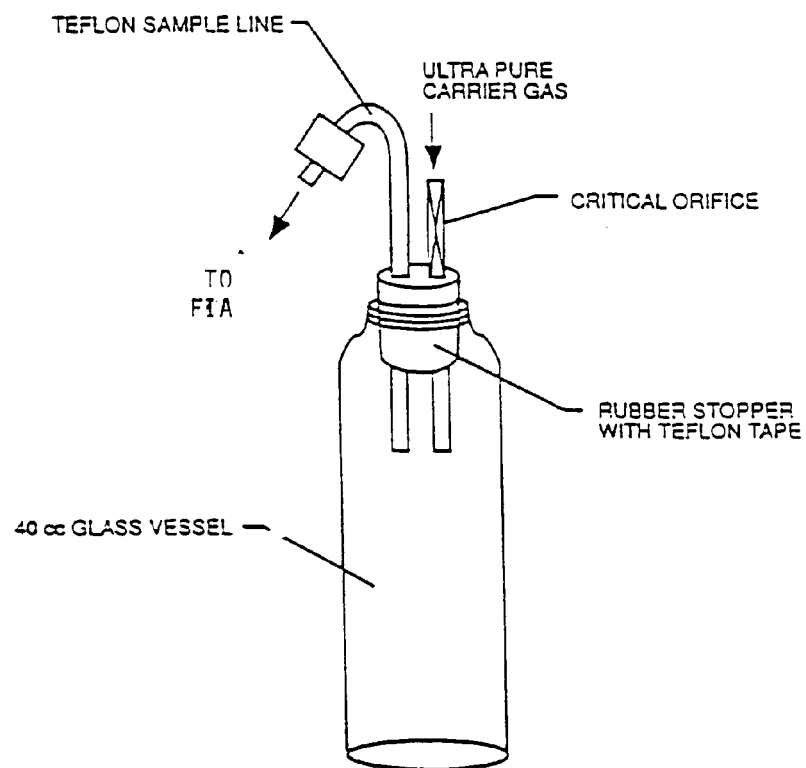Figure 204A-1. Liquid analysis sample system

TEFLON SAMPLE LINE

ULTRA PURE
CARRIER GAS

CRITICAL ORIFICE

TO
FIA

RUBBER STOPPER
WITH TEFLON TAPE
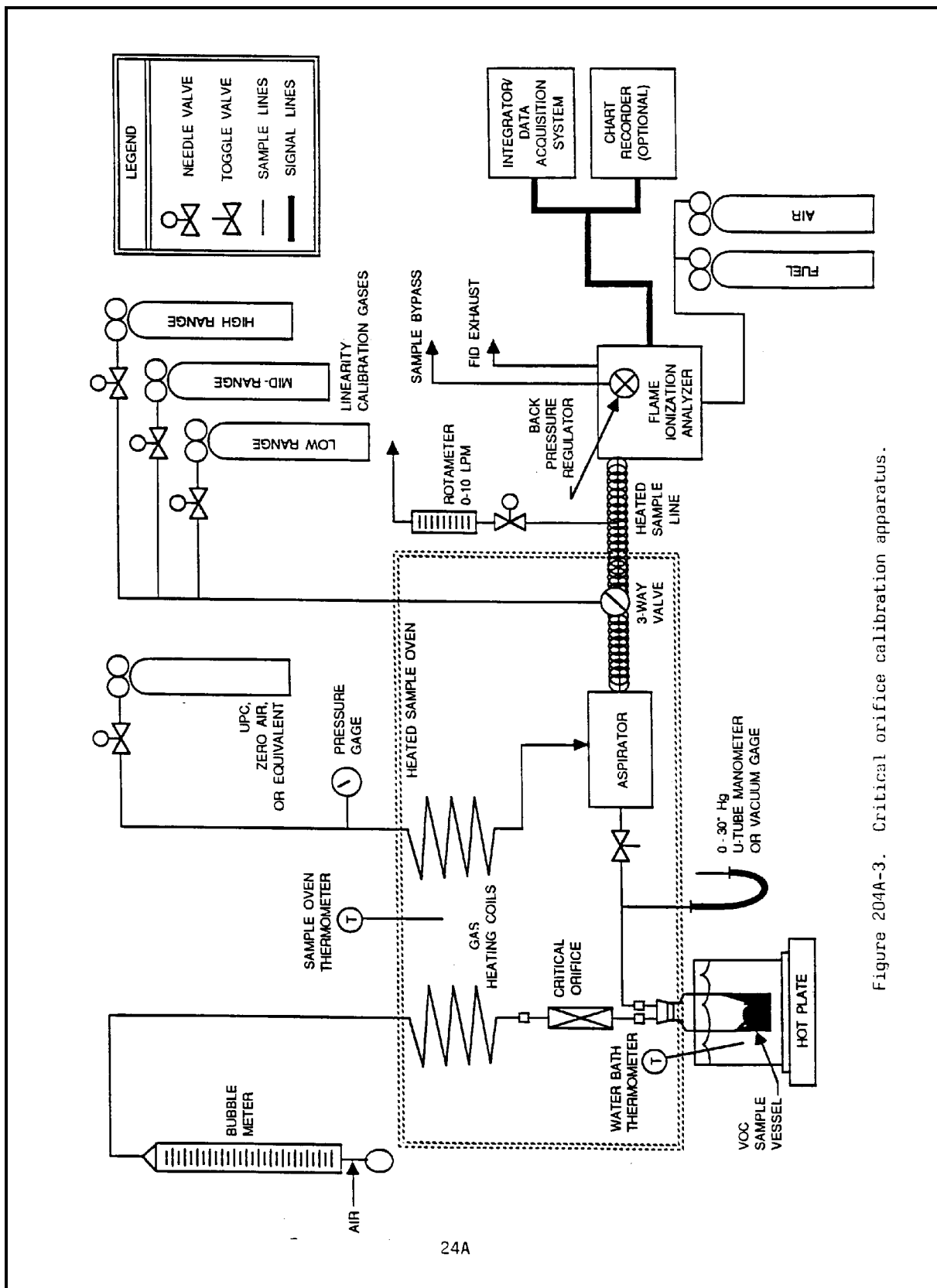
40 cc GLASS VESSEL

Figure 204A-2. VOC sampling vessel.

24

Figure 204A-3. Critical orifice calibration apparatus.

24A